



US009122158B2

(12) **United States Patent**  
**Asai**

(10) **Patent No.:** **US 9,122,158 B2**  
(45) **Date of Patent:** **Sep. 1, 2015**

(54) **PHOTO-CURABLE RESIN COMPOSITION,  
PHOTO-CURABLE DRY FILM, PATTERNING  
PROCESS, PROTECTIVE FILM, AND  
ELECTRIC/ELECTRONIC PART**

(71) Applicant: **Shin-Etsu Chemical Co., Ltd.**, Tokyo  
(JP)

(72) Inventor: **Satoshi Asai**, Annaka (JP)

(73) Assignee: **SHIN-ETSU CHEMICAL CO., LTD.**,  
Tokyo (JP)

(\*) Notice: Subject to any disclaimer, the term of this  
patent is extended or adjusted under 35  
U.S.C. 154(b) by 0 days.

(21) Appl. No.: **13/932,621**

(22) Filed: **Jul. 1, 2013**

(65) **Prior Publication Data**

US 2014/0220483 A1 Aug. 7, 2014

(30) **Foreign Application Priority Data**

Feb. 1, 2013 (JP) ..... 2013-018067

(51) **Int. Cl.**  
**G03F 7/075** (2006.01)  
**G03F 7/38** (2006.01)  
**G03F 7/004** (2006.01)

(52) **U.S. Cl.**  
CPC ..... **G03F 7/0757** (2013.01); **G03F 7/0045**  
(2013.01); **G03F 7/38** (2013.01)

(58) **Field of Classification Search**  
CPC ..... G03F 7/0757; G03F 7/38; G03F 7/0045  
USPC ..... 430/18, 270.1, 280.1, 325, 330  
See application file for complete search history.

(56) **References Cited**

U.S. PATENT DOCUMENTS

6,590,010 B2 7/2003 Kato et al.  
7,785,766 B2 8/2010 Kato et al.  
2011/0076465 A1\* 3/2011 Takeda et al. .... 428/195.1

FOREIGN PATENT DOCUMENTS

JP 6-273936 A \* 9/1994  
JP 2002-088158 A 3/2002  
JP 2008-026660 A 2/2008  
JP 2008-184571 A 8/2008  
JP 2012-103688 A 5/2012  
WO 2010/064631 A1 6/2010  
WO 2010/064632 A1 6/2010

OTHER PUBLICATIONS

Computer-generated translation of JP 6-273936 (Sep. 1994).  
Office Action dated May 22, 2015, issued in corresponding Japanese  
Patent Application No. 2013-018067 (4 pages).

\* cited by examiner

*Primary Examiner* — John A McPherson

(74) *Attorney, Agent, or Firm* — Westerman, Hattori,  
Daniels & Adrian, LLP

(57) **ABSTRACT**

A photo-curable resin composition comprising a silicone-  
containing polymer, a photobase generator, a solvent, and  
optionally an epoxy resin crosslinker forms a coating which  
serves as a protective film for the protection of electric/elec-  
tronic parts.

**18 Claims, No Drawings**

1

**PHOTO-CURABLE RESIN COMPOSITION,  
PHOTO-CURABLE DRY FILM, PATTERNING  
PROCESS, PROTECTIVE FILM, AND  
ELECTRIC/ELECTRONIC PART**

**CROSS-REFERENCE TO RELATED  
APPLICATION**

This non-provisional application claims priority under 35 U.S.C. §119(a) on Patent Application No. 2013-018067 filed in Japan on Feb. 1, 2013, the entire contents of which are hereby incorporated by reference.

**TECHNICAL FIELD**

This invention relates to a photo-curable resin composition comprising a silicone-containing polymer and a photobase generator, a photo-curable dry film thereof, a patterning process using the same, a film of the composition for the protection of electric/electronic parts such as substrates, circuit boards and interconnections, and an electric/electronic part. In particular, by virtue of its heat resistance, chemical resistance, insulation, and flexibility, the protective film is useful as dielectric film for semiconductor devices inclusive of re-wiring purposes, dielectric film for multilayer printed wiring boards, solder mask, isolation film for through-silicon-vias (TSVs), and cover-lay film, and in substrate laminating applications.

**BACKGROUND ART**

Prior art protective films for semiconductor devices and dielectric films for multilayer printed wiring boards utilize photosensitive polyimide, epoxy and silicone resin compositions. While many photosensitive materials are known for the protection of such substrates and wiring boards, JP-A 2002-088158 proposes a photosensitive silicone composition having the advantage of flexibility. Although this photosensitive silicone composition cures at low temperature to form a film which is reliable due to improved moisture-resistant adhesion, it has poor chemical resistance in photoresist strippers having a high dissolving power such as N-methyl-2-pyrrolidone.

JP-A 2008-184571 discloses a photosensitive silicone composition based on a silphenylene structure-bearing silicone polymer. Although this photosensitive silicone composition has improved chemical resistance in liquid photoresist strippers, it is desired to have more chemical resistance in solder flux fluid and higher reliability as the semiconductor device protective film.

Also, JP-A 2008-026660 proposes a photosensitive resin composition comprising, in combination, a polyfunctional epoxy resin, a phenolic curing agent, and a photoacid generator in the form of a phosphate anion-containing sulfonium salt. This resin composition can form a pattern having a high aspect ratio, but suffers from a substantial internal stress. It is desired to tailor the resin composition to be more flexible.

For the purpose of forming patterns using photosensitive resins, development works are widely made on a radical polymerization system utilizing a photo-radical generator for chain polymerization of vinyl groups and a cation polymerization system utilizing a photoacid generator. These systems, however, have several problems. First in the radical polymerization system, since the reaction is inhibited by airborne oxygen, a special measure for shutting off oxygen is necessary. In the cation polymerization system, strong acid generated is neutralized with a minute amount of airborne

2

basic substance, whereby the pattern profile is degraded. If the generated acid is left even after curing, it causes corrosion to semiconductor devices or modifies the cured film to detract from its properties.

**CITATION LIST**

Patent Document 1: JP-A 2002-088158

Patent Document 2: JP-A 2008-184571 (U.S. Pat. No. 7,785,766)

Patent Document 3: JP-A 2008-026660

**DISCLOSURE OF INVENTION**

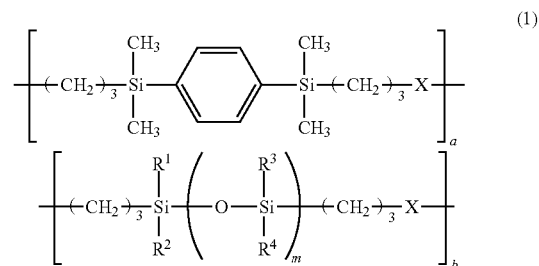
An object of the invention is to provide a photo-curable resin composition comprising a silicone-containing polymer and a photobase generator, which can be simply processed to form a pattern and cured into a film having improved characteristics, especially adhesion to substrates such as circuit boards, the cured film having good reliability as a protective film for electric/electronic parts and copper migration resistance. Another object is to provide a patterning process using the composition, a protective film of the composition for the protection of electric/electronic parts, and an electric/electronic part comprising the protective film.

The inventors have found that a photo-curable resin composition comprising a silicone-containing polymer comprising recurring units of the general formula (1), shown below, and having a weight average molecular weight of 3,000 to 500,000, a photobase generator having the general formula (4), shown below, a solvent, and optionally an epoxy resin crosslinker forms a coating which effectively serves as a protective film for the protection of electric/electronic parts. While the photobase generator of formula (4) is decomposed with radiation of wavelength 190 to 500 nm to generate a base, the photo-curable resin composition forms a coating which can be processed into a pattern by the process to be described later.

A cured film obtained from the photo-curable resin composition or from a curable dry film of the composition by a patterning process has improved properties including substrate adhesion, heat resistance, electrical insulation, reliability (when the film is used as dielectric protective film), copper migration resistance, and amenability to the substrate lamination application.

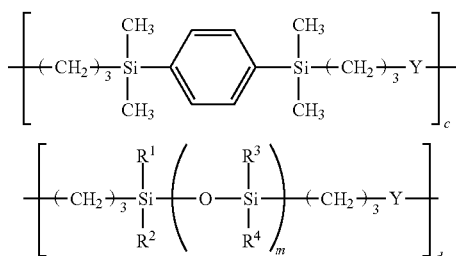
In a first aspect, the invention provides a photo-curable resin composition comprising

(A) a silicone-containing polymer comprising recurring units of the general formula (1) and having a weight average molecular weight of 3,000 to 500,000,

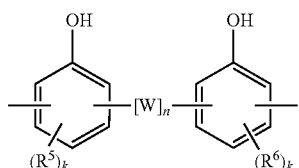


3

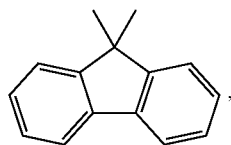
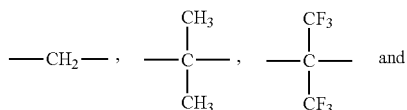
-continued



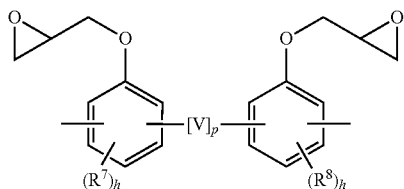
wherein R<sup>1</sup> to R<sup>4</sup> are each independently a monovalent C<sub>1</sub>-C<sub>8</sub> hydrocarbon group, m is an integer of 1 to 100, a, b, c and d each are 0 or a positive number, a+b+c+d=1, x is a divalent organic group of the general formula (2), and Y is a divalent organic group of the general formula (3),



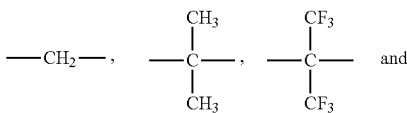
wherein W is a divalent organic group selected from the following:



n is 0 or 1, R<sup>5</sup> and R<sup>6</sup> are each independently a C<sub>1</sub>-C<sub>4</sub> alkyl or alkoxy group, k is independently 0, 1 or 2,

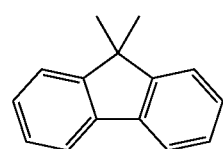


wherein V is a divalent organic group selected from the following:



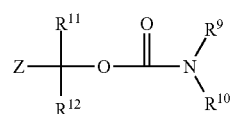
4

-continued

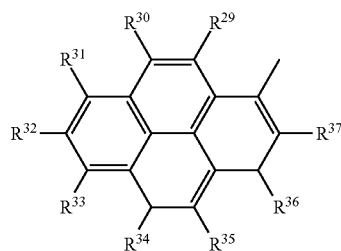
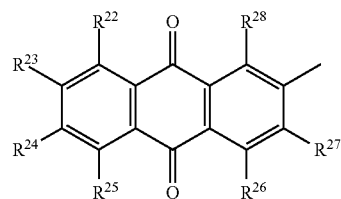
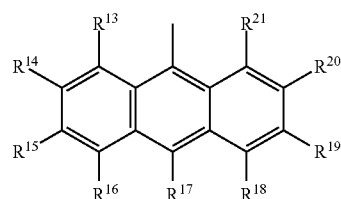


p is 0 or 1, R<sup>7</sup> and R<sup>8</sup> are each independently a C<sub>1</sub>-C<sub>4</sub> alkyl or alkoxy group, and h is independently 0, 1 or 2,

(B) a photobase generator of the general formula (4) which is decomposed with radiation of wavelength 190 to 500 nm to generate a base,

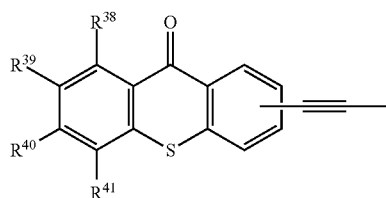


wherein R<sup>9</sup> and R<sup>10</sup> are each independently hydrogen or a straight, branched or cyclic C<sub>1</sub>-C<sub>10</sub> alkyl group, or R<sup>9</sup> and R<sup>10</sup> may bond together to form a nitrogen-containing aliphatic or aromatic ring of 3 to 8 carbon atoms with the nitrogen atom to which they are attached, which ring may have a substituent or contain a heteroatom, R<sup>11</sup> and R<sup>12</sup> are each independently hydrogen, a straight, branched or cyclic C<sub>1</sub>-C<sub>10</sub> alkyl group or an optionally substituted phenyl group, Z is a monovalent organic group selected from the general formulae (Z-1) to (Z-5):

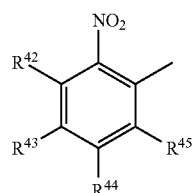


5

-continued



(Z-4)



(Z-5)

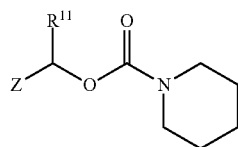
wherein  $R^{13}$  to  $R^{45}$  are each independently selected from the class consisting of hydrogen, halogen, an optionally substituted, straight, branched or cyclic  $C_1$ - $C_{10}$  alkyl group, optionally substituted  $C_1$ - $C_6$  alkoxy group, optionally substituted  $C_2$ - $C_6$  alkenyl group, optionally substituted  $C_2$ - $C_6$  alkynyl group, and optionally substituted  $C_6$ - $C_{10}$  aryl group, and

(C) a solvent.

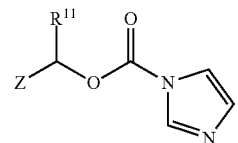
Preferably, in formula (1), c and d are not equal to 0 at the same time, and  $0 < (c+d) \leq 1.0$ .

The composition may further comprise (D) an epoxy compound containing on average at least two epoxy groups per molecule other than component (A) as crosslinker.

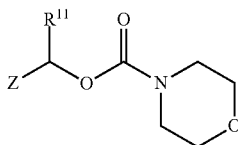
Preferably, the photobase generator having formula (4) is selected from the general formulae (4-11) to (4-13).



(4-11)



(4-12)

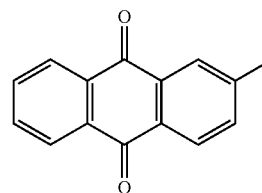


(4-13)

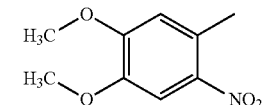
Herein Z is as defined above,  $R^{11}$  is hydrogen, a straight, branched or cyclic  $C_1$ - $C_{10}$  alkyl group or an optionally substituted phenyl group.

Also preferably, in formula (4), Z is a group having the following formula (Z-11) or (Z-12).

6

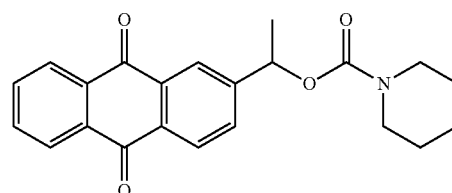


(Z-11)

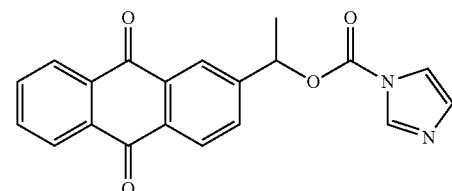


(Z-12)

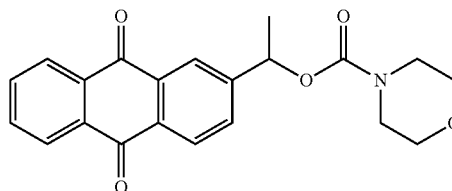
More preferably, the photobase generator having formula (4) is selected from the following formulae (4-1) to (4-4).



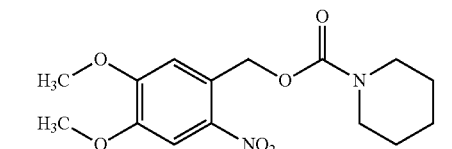
(4-1)



(4-2)



(4-3)



(4-4)

In a second aspect, the invention provides a photo-curable dry film obtained by coating and drying the photo-curable resin composition defined above to a support film.

In a third aspect, the invention provides a pattern forming process comprising the steps of (i) applying the photo-curable resin composition defined above or the photo-curable dry film defined above to a substrate to form a photo-curable resin layer thereon, (ii) exposing the photo-curable resin layer to radiation of wavelength 190 to 500 nm through a photomask, (iii) baking the exposed resin layer and developing it in a developer, and optionally, (iv) of post-curing the patterned resin layer at a temperature of 100 to 250° C.

In a fourth aspect, the invention provides a film for the protection of electric and electronic parts, which is the cured layer obtained by the process defined above.

Also contemplated herein is an electric or electronic part comprising the protective film defined above.

#### Advantageous Effects of Invention

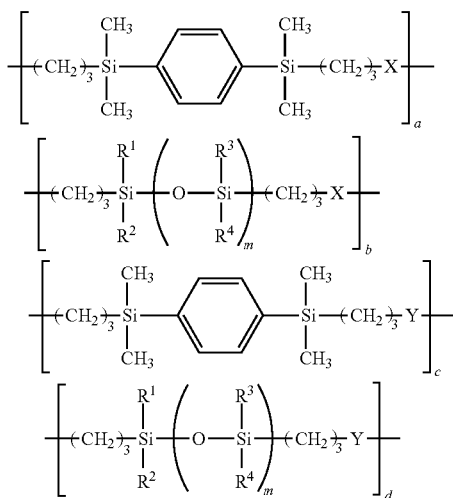
The photo-curable resin composition comprising a silicone-containing polymer and a photobase generator is subjected to photo-imaging steps to form a pattern and heat treated at a relatively low temperature of up to 250° C. The resulting patterned film has improved properties including adhesion to substrates such as electronic parts, semiconductor chips and circuit boards, mechanical properties, electrical insulation, reliability as dielectric protective film, especially copper migration resistance, crack resistance as protective film, and chemical resistance in solder flux fluid as solder protective film. The composition is advantageously used in forming protective films for electric and electronic parts including circuit boards, semiconductor chips and display devices and amenable to the substrate lamination application.

#### DESCRIPTION OF EMBODIMENTS

As used herein, the singular forms “a,” “an” and “the” include plural referents unless the context clearly dictates otherwise. “Optional” or “optionally” means that the subsequently described event or circumstances may or may not occur, and that description includes instances where the event or circumstance occurs and instances where it does not. For example, an optionally substituted alkyl group means that the alkyl group may have one or more substituents. The notation (C<sub>n</sub>-C<sub>m</sub>) means a group containing from n to m carbon atoms per group. The terms “coating,” “layer” and “film” are interchangeable.

The acronym “PBG” stands for photobase generator, “PAG” for photoacid generator, “PEB” for post-exposure bake, “Mw” for weight average molecular weight, and “GPC” for gel permeation chromatography.

One embodiment of the invention is a photo-curable resin composition comprising components (A), (B) and (C). Component (A) is a silicone-containing polymer (or high molecular weight compound) comprising recurring units of the general formula (1) and having a weight average molecular weight of 3,000 to 500,000.



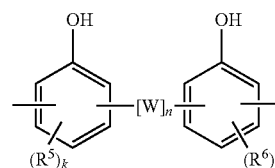
Herein each of R<sup>1</sup> to R<sup>4</sup>, which may be the same or different, stands for a monovalent hydrocarbon group having 1 to 8 carbon atoms, and preferably 1 to 6 carbon atoms. Examples include straight, branched or cyclic alkyl groups such as methyl, ethyl, propyl, isopropyl, n-butyl, tert-butyl, and cyclohexyl, straight, branched or cyclic alkenyl groups such as vinyl, allyl, propenyl, butenyl, hexenyl, and cyclohexenyl, aryl groups such as phenyl and tolyl, and aralkyl groups such as benzyl and phenylethyl.

From the standpoints of compatibility with a crosslinking agent and a photobase generator to be described later and photo-curability, m is an integer of 1 to 100, preferably 1 to 80. From the standpoints of substrate adhesion, electrical properties, and reliability, a, b, c and d each are 0 or a positive number, with the proviso that a+b+c+d=1, preferably 0<(c+d)≤1.0. Where either one of a and b is included, the subscripts preferably satisfy the range: 0.05≤(c+d)≤0.7, more preferably 0.05≤(c+d)≤0.5, and 0.3≤(a+b)≤0.95, more preferably 0.5≤(a+b)≤0.95.

The preferred ranges are: 0≤c<1, more preferably 0<c<0.7, and even more preferably 0<c<0.5; 0≤d<1, more preferably 0<d<0.7, and even more preferably 0<d<0.5. Also, the preferred ranges are: 0≤a<1, more preferably 0≤a≤0.9; and 0≤b<1, more preferably 0≤b≤0.9.

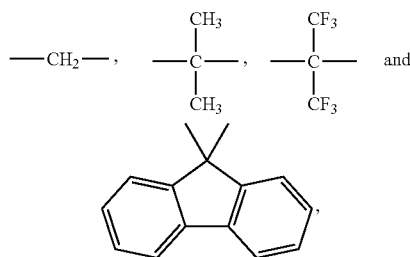
Where both a and b are 0, the preferred ranges are: 0≤c≤1, 0≤d≤1, and c+d=1, more preferably 0.3≤c≤0.7 and 0.3≤d≤0.7.

X is a divalent organic group of the general formula (2). Y is a divalent organic group of the general formula (3). It is noted that component (A) contains at least one divalent organic group of formula (2) or (3).



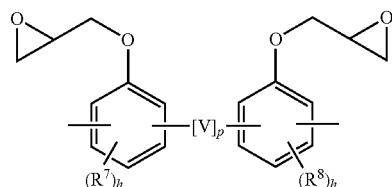
(2)

Herein W is a divalent organic radical selected from the following:

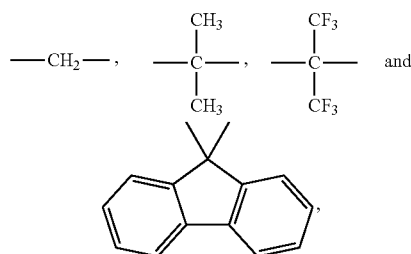


n is 0 or 1, each of R<sup>5</sup> and R<sup>6</sup> which may be the same or different is a C<sub>1</sub>-C<sub>4</sub> alkyl or alkoxy group, and k is independently 0, 1 or 2. Examples of R<sup>5</sup> and R<sup>6</sup> include methyl, ethyl, isopropyl, tert-butyl, methoxy, ethoxy, and isopropoxy.

9



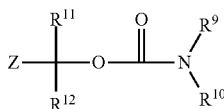
Herein V is a divalent organic radical selected from the following:



p is 0 or 1, each of  $R^7$  and  $R^8$  which may be the same or different is a  $C_1$ - $C_4$  alkyl or alkoxy group, and h is independently 0, 1 or 2. Examples of  $R^7$  and  $R^8$  are as exemplified for  $R^5$  and  $R^6$ .

The silicone-containing polymer should have a Mw of 3,000 to 500,000 and preferably 5,000 to 300,000, from the standpoints of compatibility and photo-curability of a composition comprising the polymer as well as mechanical properties of the cured composition. It is noted that Mw is determined by GPC versus polystyrene standards.

Component (B) is a photobase generator which is decomposed with radiation of wavelength 190 to 500 nm to generate an amine-containing base, which serves as a catalyst for the resin or silicone-containing polymer (A) to undergo crosslinking reaction. The PBG is represented by the general formula (4).



Herein  $R^9$  and  $R^{10}$  are each independently hydrogen, or a straight, branched or cyclic  $C_1$ - $C_{10}$  alkyl group, or  $R^9$  and  $R^{10}$  may bond together to form a nitrogen-containing aliphatic ring or nitrogen-containing aromatic ring of 3 to 8 carbon atoms with the nitrogen atom to which they are attached, which ring may have a substituent or contain a heteroatom.

In formula (4), examples of the straight, branched or cyclic  $C_1$ - $C_{10}$  alkyl group represented by  $R^9$  and  $R^{10}$  include methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl, tert-butyl, cyclobutyl, n-pentyl, isopentyl, sec-pentyl, tert-pentyl, neopentyl, 2-methylbutyl, 1,2-dimethylpropyl, 1-ethylpropyl, cyclopentyl, n-hexyl, isohexyl, sec-hexyl, tert-hexyl, neohexyl, 2-methylpentyl, 1,2-dimethylbutyl, 2,3-dimethylbutyl, 1-ethylbutyl, cyclohexyl, n-heptyl, isoheptyl, sec-heptyl, tert-heptyl, neoheptyl, cycloheptyl, n-octyl, isooctyl, sec-octyl, tert-octyl, neooctyl, 2-ethylhexyl, cyclooctyl, n-nonyl, isononyl, sec-nonyl, tert-nonyl, neononyl, cyclononyl, n-de-

10

cyl, isodecyl, sec-decyl, tert-decyl, neodecyl, cyclodecyl, norbornyl, and adamantyl. Of these, straight, branched or cyclic alkyl groups of 1 to 8 carbon atoms are preferred, examples of which include methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl, tert-butyl, cyclobutyl, n-pentyl, isopentyl, sec-pentyl, tert-pentyl, neopentyl, 2-methylbutyl, 1,2-dimethylpropyl, 1-ethylpropyl, cyclopentyl, n-hexyl, isohexyl, sec-hexyl, tert-hexyl, neohexyl, 2-methylpentyl, 1,2-dimethylbutyl, 2,3-dimethylbutyl, 1-ethylbutyl, cyclohexyl, n-heptyl, isoheptyl, sec-heptyl, tert-heptyl, neoheptyl, cycloheptyl, n-octyl, isooctyl, sec-octyl, tert-octyl, neooctyl, 2-ethylhexyl, and cyclooctyl. Straight or cyclic alkyl groups of 1 to 8 carbon atoms are more preferred, examples of which include methyl, ethyl, n-propyl, n-butyl, cyclobutyl, n-pentyl, cyclopentyl, n-hexyl, cyclohexyl, n-heptyl, cycloheptyl, n-octyl, and cyclooctyl. Inter alia, straight or cyclic alkyl groups of 1 to 6 carbon atoms are most preferred, examples of which include methyl, ethyl, n-propyl, n-butyl, cyclobutyl, n-pentyl, cyclopentyl, n-hexyl, and cyclohexyl.

Alternatively, in formula (4),  $R^9$  and  $R^{10}$  bond together to form a nitrogen-containing aliphatic or aromatic ring of 3 to 8 carbon atoms with the nitrogen atom to which they are attached, which ring may have a substituent or contain a heteroatom. As used herein, the phrase "to form a nitrogen-containing aliphatic or aromatic ring of 3 to 8 carbon atoms" means that  $R^9$  and  $R^{10}$  bond together to form a saturated or unsaturated alkylene group (saturated or unsaturated alkanediyl group) having two valence bonds to bond with the nitrogen atom, and specifically a saturated or unsaturated alkylene group (saturated or unsaturated alkanediyl group) of 3 to 8 carbon atoms which may contain a heteroatom such as nitrogen, sulfur or oxygen in the chain.

Examples of the saturated or unsaturated alkylene group (saturated or unsaturated alkanediyl group) of 3 to 8 carbon atoms which may contain a heteroatom in the chain include straight or branched, saturated alkylene group (saturated alkanediyl group) of 3 to 8 carbon atoms, free of heteroatom, such as trimethylene, tetramethylene, pentamethylene, hexamethylene, heptamethylene, octamethylene, 1,4-dimethyltetramethylene, 1,5-dimethylpentamethylene, and 1,3,5-trimethylpentamethylene; straight or branched, saturated alkylene group (saturated alkanediyl group) of 3 to 8 carbon atoms which contains a heteroatom (e.g., oxygen, sulfur) in the chain such as methyleneoxydimethylene (methyleneoxyethylene), methylenethiodimethylene (methylenethioethylene), dimethyleneoxydimethylene (ethyleneoxyethylene), dimethylenethiodimethylene (ethylenethioethylene), 1,1',2-trimethyl-methyleneoxydimethylene (1,1',2-trimethyl-methyleneoxyethylene), 1,1',2-trimethyl-methylenethiodimethylene (1,1',2-trimethyl-methylenethioethylene), 1,1',2,2'-tetramethyl-dimethyleneoxydimethylene (1,1',2,2'-tetramethyl-ethyleneoxyethylene), 1,1',2,2'-tetramethyl-dimethylenethiodimethylene (1,1',2,2'-tetramethyl-ethylenethioethylene); straight or branched, unsaturated alkylene group (unsaturated alkanediyl group) of 4 to 8 carbon atoms, free of heteroatom, such as buta-1,3-diene-1,4-diyl, 1,4-dimethyl-but-1,3-diene-1,4-diyl, and 1,4-diethyl-but-1,3-diene-1,4-diyl; straight or branched, unsaturated alkylene group (unsaturated alkanediyl group) of 3 to 8 carbon atoms which contains a heteroatom (e.g., nitrogen) such as 2-aza-but-1,3-diene-1,4-diyl, 1,4-dimethyl-2-aza-but-1,3-diene-1,4-diyl, 1,4-diethyl-2-aza-but-1,3-diene-1,4-diyl, 1-aza-but-1,3-diene-1,4-diyl, 2,4-dimethyl-1-aza-but-1,3-diene-1,4-diyl, and 2,4-diethyl-1-aza-but-1,3-diene-1,4-diyl.

Where " $R^9$  and  $R^{10}$  bond together to form a nitrogen-containing aliphatic or aromatic ring of 3 to 8 carbon atoms

## 11

with the nitrogen atom to which they are attached, which ring may have a substituent or contain a heteroatom," suitable substituents include substituents (or functional groups) other than hydrocarbon, attached to the "nitrogen-containing aliphatic or aromatic ring" such as, for example, hydroxyl, mercapto, cyano, nitro, and halogen (e.g., fluoro, chloro, bromo or iodo).

Where "R<sup>9</sup> and R<sup>10</sup> bond together to form a nitrogen-containing aliphatic or aromatic ring of 3 to 8 carbon atoms with the nitrogen atom to which they are attached, which ring may have a substituent or contain a heteroatom," the number of carbon atoms is the number of carbon atoms that constitute the nitrogen-containing aliphatic or aromatic ring, with the carbon atom in the substituent (e.g., cyano) being excluded.

In the compound of formula (4) wherein "R<sup>9</sup> and R<sup>10</sup> bond together to form a nitrogen-containing aliphatic or aromatic ring of 3 to 8 carbon atoms with the nitrogen atom to which they are attached, which ring may have a substituent or contain a heteroatom," examples of the nitrogen-containing aliphatic or aromatic ring of 3 to 8 carbon atoms, that is, amine partial structure include nitrogen-containing aliphatic rings of 3 to 8 carbon atoms such as azetidine (4-membered ring), pyrrolidine (5-membered ring), piperidine (6-membered ring), hexamethyleneimine (azepane, 7-membered ring), heptamethyleneimine (azocane, 8-membered ring), and octamethyleneimine (azonane, 9-membered ring); nitrogen-containing aliphatic ring of 3 to 8 carbon atoms having hydrogen (bonded to a carbon atom within the aliphatic ring) substituted by methyl, such as 2,5-dimethylpyrrolidine (5-membered ring), 2,6-dimethylpiperidine (6-membered ring), and 2,4,6-trimethylpiperidine (6-membered ring); nitrogen-containing aliphatic rings of 3 to 8 carbon atoms containing a heteroatom (e.g., oxygen, sulfur) other than nitrogen in the chain such as oxazolidine (5-membered ring), thiazolidine (5-membered ring), morpholine (6-membered ring) and thiomorpholine (6-membered ring); nitrogen-containing aliphatic ring of 4 to 8 carbon atoms having hydrogen (bonded to a carbon atom within the aliphatic ring) substituted by methyl and containing a heteroatom (e.g., oxygen, sulfur) other than nitrogen in the chain, such as 2,3,5,6-tetramethylmorpholine (6-membered ring) and 2,3,5,6-tetramethylthiomorpholine (6-membered ring); nitrogen-containing aromatic ring of 3 to 4 carbon atoms such as pyrrole (5-membered ring), imidazole (5-membered ring) and pyrazole (5-membered ring); nitrogen-containing aromatic ring of 4 to 8 carbon atoms having hydrogen (bonded to a carbon atom within the aromatic ring) substituted by methyl or ethyl, such as 2,5-dimethylpyrrole (5-membered ring), 2,5-diethylpyrrole (5-membered ring), 2,5-dimethylimidazole (5-membered ring), 2,5-diethylimidazole (5-membered ring), 3,5-dimethylpyrazole (5-membered ring), and 3,5-diethylpyrazole (5-membered ring).

Namely, nitrogen-containing aliphatic or aromatic rings of 3 to 8 carbon atoms having hydrogen (bonded to a carbon atom within the aliphatic or aromatic ring) substituted by methyl or ethyl and nitrogen-containing aliphatic rings of 3 to 8 carbon atoms containing a heteroatom (e.g., oxygen, sulfur) other than nitrogen in the chain are also included in the concept of "nitrogen-containing aliphatic or aromatic rings of 3 to 8 carbon atoms."

Further the "nitrogen-containing aliphatic or aromatic ring of 3 to 8 carbon atoms" may have a substituent (or functional group) other than hydrocarbon. Examples of the substituent include, as mentioned above, hydroxyl, mercapto, cyano, nitro, and halogen (e.g., fluoro, chloro, bromo or iodo). Examples of the nitrogen-containing aliphatic or aromatic

## 12

ring of 3 to 8 carbon atoms having a substituent include, but are not limited to, 4-hydroxypiperidine (6-membered ring), 4-mercaptopiperidine (6-membered ring), 4-cyanopiperidine (6-membered ring), 4-nitropiperidine (6-membered ring), 4-chloropiperidine (6-membered ring), and 4-bromopiperidine (6-membered ring).

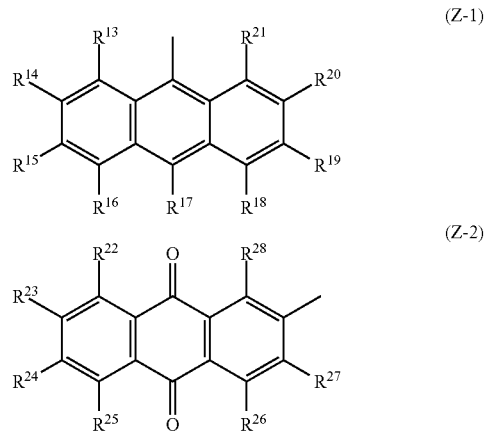
For a combination of R<sup>9</sup> and R<sup>10</sup> in formula (4), it is preferred that R<sup>9</sup> be hydrogen and R<sup>10</sup> be a straight or cyclic C<sub>3</sub>-C<sub>8</sub> alkyl group, that both R<sup>9</sup> and R<sup>10</sup> be straight C<sub>1</sub>-C<sub>8</sub> alkyl, and that R<sup>9</sup> and R<sup>10</sup> bond together to form a nitrogen-containing aliphatic or aromatic ring of 3 to 7 carbon atoms with the nitrogen atom to which they are attached, which ring may have a substituent. It is more preferred that R<sup>9</sup> be hydrogen and R<sup>10</sup> be a straight or cyclic C<sub>3</sub>-C<sub>6</sub> alkyl group, that both R<sup>9</sup> and R<sup>10</sup> be straight C<sub>1</sub>-C<sub>6</sub> alkyl, and that R<sup>9</sup> and R<sup>10</sup> bond together to form a nitrogen-containing aliphatic ring of 4 or 5 carbon atoms with the nitrogen atom to which they are attached, which ring may have a substituent.

In formula (4), R<sup>11</sup> and R<sup>12</sup> are each independently hydrogen, a straight, branched or cyclic C<sub>1</sub>-C<sub>10</sub> alkyl group or an optionally substituted phenyl group.

Examples of the straight, branched or cyclic C<sub>1</sub>-C<sub>10</sub> alkyl group represented by R<sup>11</sup> and R<sup>12</sup> include methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl, tert-butyl, cyclobutyl, n-pentyl, isopentyl, sec-pentyl, tert-pentyl, neopentyl, 2-methylbutyl, 1,2-dimethylpropyl, 1-ethylpropyl, cyclopentyl, n-hexyl, isohexyl, sec-hexyl, tert-hexyl, neo-hexyl, 2-methylpentyl, 1,2-dimethylbutyl, 2,3-dimethylbutyl, 1-ethylbutyl, cyclohexyl, n-heptyl, isoheptyl, sec-heptyl, tert-heptyl, neoheptyl, cycloheptyl, n-octyl, isooctyl, sec-octyl, tert-octyl, neooctyl, 2-ethylhexyl, cyclooctyl, n-nonyl, isononyl, sec-nonyl, tert-nonyl, neononyl, cyclononyl, n-decyl, isodecyl, sec-decyl, tert-decyl, neodecyl, cyclodecyl, norbornyl, and adamantyl. Inter alia, straight C<sub>1</sub>-C<sub>3</sub> alkyl groups are preferred, such as methyl, ethyl and n-propyl, with methyl or a C<sub>1</sub> alkyl group being most preferred.

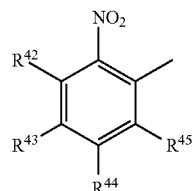
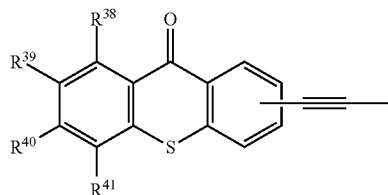
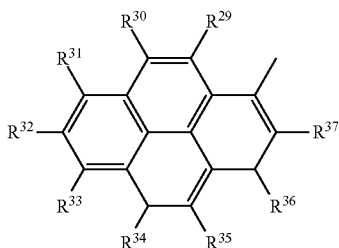
When R<sup>11</sup> and R<sup>12</sup> are an optionally substituted phenyl group, examples of the substituent include halogens such as fluorine, chlorine, bromine and iodine, and straight or branched C<sub>1</sub>-C<sub>3</sub> alkyl groups such as methyl, ethyl, n-propyl and isopropyl. Examples of the optionally substituted phenyl group include phenyl, tolyl, xylyl, mesityl, cumenyl and chlorophenyl.

In formula (4), Z is a monovalent organic group selected from the general formulae (Z-1), (Z-2), (Z-3), (Z-4) and (Z-5).



13

-continued



In formula (Z-1) to (Z-5),  $R^{13}$  to  $R^{45}$  are each independently hydrogen, halogen, an optionally substituted, straight, branched or cyclic  $C_1$ - $C_{10}$  alkyl group, optionally substituted  $C_1$ - $C_6$  alkoxy group, optionally substituted  $C_2$ - $C_6$  alkenyl group, optionally substituted  $C_2$ - $C_6$  alkynyl group, or optionally substituted  $C_6$ - $C_{10}$  aryl group.

Examples of the straight, branched or cyclic  $C_1$ - $C_{10}$  alkyl group represented by  $R^{13}$  to  $R^{45}$  include methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl, tert-butyl, cyclobutyl, n-pentyl, isopentyl, sec-pentyl, tert-pentyl, neopentyl, 2-methylbutyl, 1,2-dimethylpropyl, 1-ethylpropyl, cyclopentyl, n-hexyl, isohexyl, sec-hexyl, tert-hexyl, neohexyl, 2-methylpentyl, 1,2-dimethylbutyl, 2,3-dimethylbutyl, 1-ethylbutyl, cyclohexyl, n-heptyl, isoheptyl, sec-heptyl, tert-heptyl, neoheptyl, cycloheptyl, n-octyl, isooctyl, sec-octyl, tert-octyl, neooctyl, 2-ethylhexyl, cyclooctyl, n-nonyl, isononyl, sec-nonyl, tert-nonyl, neononyl, cyclononyl, n-decyl, isodecyl, sec-decyl, tert-decyl, neodecyl, cyclodecyl, norbornyl, and adamantyl. Inter alia, straight  $C_1$ - $C_3$  alkyl groups are preferred, such as methyl, ethyl and n-propyl, with methyl being most preferred.

Examples of the halogen represented by  $R^{13}$  to  $R^{45}$  include fluorine, chlorine, bromine and iodine. Inter alia, chlorine and bromine are preferred, with bromine being most preferred.

Suitable alkoxy groups represented by  $R^{13}$  to  $R^{45}$  include methoxy, ethoxy, n-propoxy, isopropoxy, n-butoxy, isobutoxy, sec-butoxy, and tert-butoxy. Suitable alkenyl groups include vinyl, propenyl, butenyl, pentenyl. Suitable alkynyl groups include ethynyl, propynyl, butynyl, pentynyl. Suitable aryl groups include phenyl, tolyl, naphthyl and anthryl.

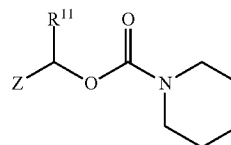
It is noted that formula (Z-4) is depicted as having an ethynyl group attached to thioxanthone ring. Herein, the ethynyl group may be attached to the carbon atom at any of 1 to 4-positions on the thioxanthone ring, preferably at 2- or 3-position, and most preferably at 2-position.

More preferably, the general formula (4) is selected from the general formulae (4-11) to (4-13).

14

(Z-3)

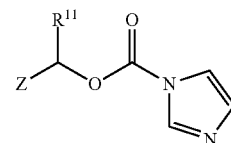
5



(4-11)

(Z-4)

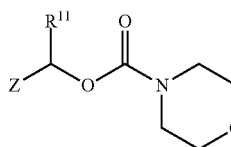
10



(4-12)

(Z-5)

15



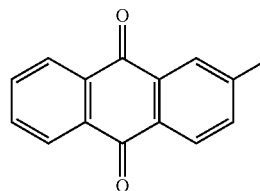
(4-13)

Herein Z is as defined and illustrated above.  $R^{11}$  is hydrogen, a straight, branched or cyclic  $C_1$ - $C_{10}$  alkyl group or an optionally substituted phenyl group, and preferably hydrogen or methyl.

In the PBG of formula (4), Z is most preferably a monovalent organic group having the following formula (Z-11) or (Z-12).

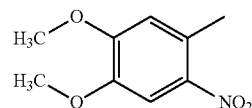
(Z-11)

35



(Z-12)

40

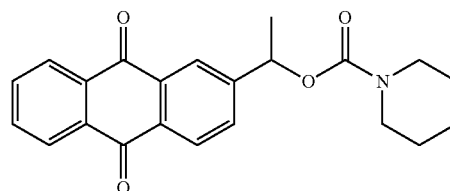


45

Of the PBGs of formula (4), those compounds having the following formulae (4-1) to (4-4) are preferred.

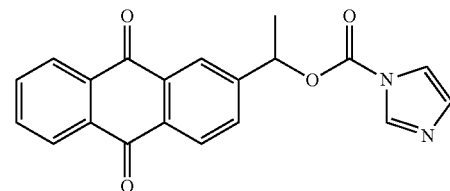
(4-1)

55



(4-2)

60

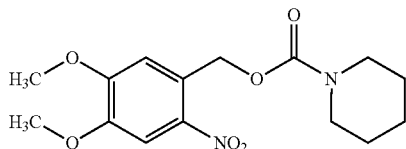
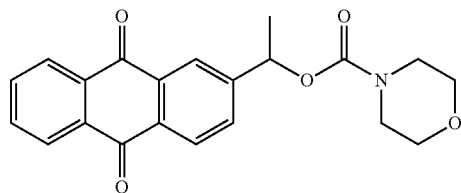


65



15

-continued



The PBGs may be used alone or in admixture of two or more. It is preferred from the standpoint of photo-curability to add the PBG in an amount of 0.05 to 25 parts by weight, and more preferably 2 to 15 parts by weight, per 100 parts by weight of the silicone-containing polymer. As long as the PBG is used within the range, a fully adherent coating is obtainable, from which a pattern can be efficiently formed.

Component (C) is a solvent. The solvent used herein may be selected from those solvents in which the silicone-containing polymer (A), PBG (B), crosslinker, and other additives (to be described later) are soluble. Typically organic solvents are used as these components are fully soluble therein.

Illustrative, non-limiting, examples of the organic solvent include ketones such as cyclohexanone, cyclopentanone and methyl-2-n-amyketone; alcohols such as 3-methoxybutanol, 3-methyl-3-methoxybutanol, 1-methoxy-2-propanol, and 1-ethoxy-2-propanol; ethers such as propylene glycol monomethyl ether, ethylene glycol monomethyl ether, propylene glycol monoethyl ether, ethylene glycol monoethyl ether, propylene glycol dimethyl ether, and diethylene glycol dimethyl ether; and esters such as propylene glycol monomethyl ether acetate (PGMEA), propylene glycol monoethyl ether acetate, ethyl lactate, ethyl pyruvate, butyl acetate, methyl 3-methoxypropionate, ethyl 3-ethoxypropionate, tert-butyl acetate, tert-butyl propionate, propylene glycol mono-tert-butyl ether acetate, and  $\gamma$ -butyrolactone. These solvents may be used alone or in combinations of two or more thereof. Of these solvents, preferred are ethyl lactate, cyclohexanone, cyclopentanone, PGMEA,  $\gamma$ -butyrolactone, and mixtures thereof, in which the photobase generator is most soluble.

An appropriate amount of the solvent (C) used is 50 to 2,000 parts, and especially 100 to 1,000 parts by weight per 100 parts by weight of components (A) and (B) combined, when determined from the standpoints of compatibility and viscosity of the photo-curable resin composition.

In a preferred embodiment, the photo-curable resin composition may further comprise (D) a crosslinker. It is an epoxy compound containing on average at least two epoxy groups per molecule other than component (A). The crosslinker induces curing reaction with the silicone-containing polymer for facilitating pattern formation and augmenting the strength of a cured product. The crosslinker should preferably have a Mw of 150 to 10,000, and more preferably 200 to 3,000, from the standpoints of photo-curability and heat resistance.

Suitable examples of the crosslinker include bisphenol epoxy resins such as bisphenol A epoxy resin and bisphenol F epoxy resin, novolak epoxy resins such as phenol novolak epoxy resin and cresol novolak epoxy resin, triphenol alkane epoxy resins and polymers thereof, biphenyl epoxy resins,

16

dicyclopentadiene-modified phenol novolak epoxy resins, phenol aralkyl epoxy resins, biphenyl aralkyl epoxy resins, naphthalene ring-containing epoxy resins, glycidyl ester epoxy resins, alicyclic epoxy resins, and heterocyclic epoxy resins. Of these, bisphenol epoxy resins and novolak epoxy resins are preferred.

The crosslinkers may be used alone or in admixture of two or more. An appropriate amount of the crosslinker used is 0 to 50 parts by weight, and if added, 0.5 to 50 parts, and especially 1 to 30 parts by weight per 100 parts by weight of the silicone-containing polymer, when determined from the standpoints of flexibility, chemical resistance and substrate adhesion. An excessive amount of crosslinker may prevent a cured film from exerting the desired properties.

In addition to the aforementioned components, the photo-curable resin composition may include optional additives. Suitable additives include a surfactant which is commonly used for improving the coating characteristics, a light absorber which is used for improving light absorption efficiency of photobase generator, and the like.

Preferred surfactants are nonionic surfactants, for example, fluorochemical surfactants such as perfluoroalkyl polyoxyethylene ethanols, fluorinated alkyl esters, perfluoroalkylamine oxides, and fluorinated organosiloxane compounds. These surfactants are commercially available. Illustrative examples include Fluorad FC-4430 from Sumitomo 3M Ltd., Surfion S-141 and S-145 from Asahi Glass Co., Ltd., Unidyne DS-401, DS-4031, and DS-451 from Daikin Industries Ltd., Megaface F-8151 from DIC Corp., and X-70-093 from Shin-Etsu Chemical Co., Ltd. Preferred surfactants include Fluorad FC-4430 from Sumitomo 3M Ltd. and X-70-093 from Shin-Etsu Chemical Co., Ltd.

Exemplary light absorbers include diaryl sulfoxides, diaryl sulfones, 9,10-dimethylantracene and 9-fluorenone.

The photo-curable resin composition of the invention is prepared in a conventional way. For example, it can be prepared by agitating and mixing the aforementioned components and optional additives in the solvent and passing the mixture through a filter to remove solid impurities, if necessary.

The photo-curable resin composition thus prepared is useful as protective films for semiconductor devices, protective films on interconnections, cover-lay films, and solder masks. It can also be applied to electrical and electronic parts, for example, as a dielectric film for TSVs.

#### Pattern Forming Process

When a pattern is formed using the photo-curable resin composition, the patterning process involves the steps of (i) applying the photo-curable resin composition to a substrate to form a photo-curable resin layer or coating thereon, (ii) exposing the layer to radiation having a wavelength of 190 to 500 nm through a photomask, (iii) post-exposure baking (PEB) and developing the exposed layer in a developer. After the layer or coating is patterned through these steps, the step (iv) of heating the patterned coating is performed for post-curing purpose, eventually yielding the desired film suitable for the protection of electric or electronic parts.

More particularly, the photo-curable resin composition is first (i) applied onto a substrate to form a photo-curable resin layer or coating thereon. The substrates used herein include silicon wafers, TSV silicon wafers, and plastic or ceramic circuit substrates. Also useful is a substrate having a metal (e.g., Cu, Ni or Au) deposited partially or entirely on its surface by ion sputtering, plating or the like.

Any well-known techniques complying with lithography may be used to apply the composition. For example, the composition is applied by dipping, spin coating or roll coat-

ing. The coverage may be determined as appropriate for a particular purpose although a coating weight sufficient to form a photo-curable resin layer of 0.1 to 100  $\mu\text{m}$  thick is often preferred. Preferably the photo-curable resin layer has a thickness of 1 to 100  $\mu\text{m}$ , more preferably 3 to 60  $\mu\text{m}$ .

In order that effective photo-curing reaction take place, the solvent may be previously evaporated off by preheating or prebaking, if necessary. The prebaking is, for example, at 40 to 140° C. for 1 minute to 1 hour.

The coating is then (ii) exposed to radiation having a wavelength of 190 to 500 nm through a photomask for effecting photo-curing reaction. The photomask used herein may be a member in which a desired pattern has been cut out. The photomask is preferably made of a material capable of shielding the radiation of wavelength 190 to 500 nm, for example, chromium although the photomask material is not limited thereto. Examples of the radiation of wavelength 190 to 500 nm include radiation of various wavelengths generated by radiation-emitting units, for example, UV radiation (e.g., g, h and i-line) and deep UV radiation (248 nm, 198 nm). A wavelength range from 248 to 436 nm is preferred. An appropriate exposure dose is 100 to 8,000 mJ/cm<sup>2</sup>.

If desired for increasing the development sensitivity, the exposed coating (or layer) may be heat treated (iii). Such post-exposure baking (PEB) is effected, for example, at 40 to 140° C. for 0.5 to 10 minutes.

Following the exposure and PEB, the coating (or layer) is developed in a developer. The developer is preferably any of customarily used organic solvents, for example, alcohols such as isopropyl alcohol (IPA), ketones such as cyclohexanone, glycols such as propylene glycol monomethyl ether, and esters such as PGMEA. The solvent which may be used as the solvent for the photo-curable resin composition can be used at the development stage. Development is effected in a conventional manner, for example, by dipping the pattern-bearing substrate in the developer. The development is followed by washing, rinsing and drying if necessary. There is obtained a coating or film of photo-curable resin composition having the desired pattern. As a result of development, the unexposed area of film is dissolved away while the area of film which has been crosslinked via exposure is left as a pattern.

Although the pattern forming process has been described, it is sometimes unnecessary to form a pattern. When it is simply desired to form a uniform film, for example, the same process as above may be followed except that the resin layer is exposed to radiation of wavelength 190 to 500 nm without photomask (flood exposure).

If desired, the patterned coating may be post-cured (iv) by heating in an oven or on a hot plate at a temperature of 100 to 250° C., preferably 150 to 220° C. Post-curing at 100 to 250° C. is effective for increasing the crosslinking density of the coating and removing the residual volatile matter. The resulting coating has augmented adhesion to substrates, heat resistance, high strength and good electrical properties. The post-curing time may range from 10 minutes to 10 hours.

Since the cured coating (or film) obtained from the photo-curable resin composition in the above-described way has heat resistance, flexibility, electrical insulation, mechanical properties, substrate adhesion, and chemical resistance in solder flux fluid, it can be advantageously used as a protective film on electric and electronic parts such as semiconductor devices.

#### Photo-Curable Dry Film

A further embodiment of the invention is a photo-curable dry film comprising a photo-curable resin layer sandwiched between a support film and a protective film wherein the

photo-curable resin layer is formed by applying and drying the photo-curable resin composition defined above to the support film.

The photo-curable dry film is solid, and the photo-curable resin layer contains no solvent. This eliminates the risk that bubbles resulting from volatilization of solvent are left within the resin layer and between the resin layer and the rugged substrate surface. An appropriate thickness range exists for the layer when planarity and step coverage on rugged substrate surface and a substrate lamination spacing are taken into account. It is preferred from the standpoints of planarity, step coverage, and substrate lamination spacing that the photo-curable resin layer have a thickness of 5 to 300  $\mu\text{m}$ , more preferably 10 to 150  $\mu\text{m}$ .

Furthermore, the viscosity and fluidity of the photo-curable resin layer are closely correlated. As long as the photo-curable resin layer has a proper range of viscosity, it exhibits a sufficient fluidity to fill deeply even in a narrow gap or it softens to enhance the adhesion to the substrate. Accordingly, from the standpoint of fluidity, the photo-curable resin layer should preferably have a viscosity in the range of 10 to 5,000 Pa-s, more preferably 20 to 2,000 Pa-s, and even more preferably 20 to 1,000 Pa-s at a temperature of 80 to 120° C. It is noted that the viscosity is measured by a rheometer HAAKE MARS II.

The photo-curable dry film has the advantage that when tightly attached to a substrate having asperities on its surface, the photo-curable resin layer is coated so as to conform to the asperities, achieving high planarity. Particularly when the photo-curable resin layer is composed mainly of a photo-curable silicone composition as defined herein, higher planarity is achievable owing to the advantage of low surface tension. Further, if the photo-curable resin layer is in close contact with the substrate in a vacuum environment, generation of gaps therebetween is effectively inhibited.

Next, it is described how to manufacture the photo-curable dry film. An apparatus for manufacturing the photo-curable dry film may be a film coater commonly used in the manufacture of pressure-sensitive adhesive products. Suitable film coaters include, for example, a comma coater, comma reverse coater, multiple coater, die coater, lip coater, lip reverse coater, direct gravure coater, offset gravure coater, three roll bottom reverse coater, and four roll bottom reverse coater.

The support film is unwound from a supply roll in the film coater, passed across the head of the film coater where the photo-curable resin composition is coated onto the support film to the predetermined buildup, and then moved through a hot air circulating oven at a predetermined temperature for a predetermined time, where the photo-curable resin layer is dried on the support film. Thereafter, the support film having the photo-curable resin layer thereon and a protective film which is unwound from another supply roll in the film coater are passed across a laminate roll under a predetermined pressure whereby the protective film is bonded to the photo-curable resin layer on the support film, whereupon the laminate is wound up on a take-up shaft in the film coater. Preferably, the oven temperature is 25 to 150° C., the pass time is 1 to 100 minutes, and the bonding pressure is 0.01 to 5 MPa.

The support film used in the photo-curable dry film may be a single film or a multilayer film consisting of a plurality of stacked polymer layers. Examples of the film material include synthetic resins such as polyethylene, polypropylene, polycarbonate and polyethylene terephthalate (PET), with the PET film being preferred for appropriate flexibility, mechanical strength and heat resistance. These films may have been pretreated such as by corona treatment or coating of a release

19

agent. Such films are commercially available, for example, Cerapeel® WZ(RX) and Cerapeel® BX8(R) from Toray Advanced Film Co., Ltd.; E7302 and E7304 from Toyobo Co., Ltd.; Purex® G31 and Purex® G71T1 from Teijin DuPont Films Japan Ltd.; and PET 38×1-A3, PET38×1-V8 and PET38×1-X08 from Nippa Co., Ltd.

The protective film used in the photo-curable dry film may be similar to the support film. Among others, PET and polyethylene films having an appropriate flexibility are preferred. Such films are also commercially available. For example, PET films are as mentioned above, and polyethylene films include GF-8 from Tamapoly Co., Ltd. and PE film 0 type from Nippa Co., Ltd.

Both the support and protective films preferably have a thickness of 10 to 100 μm, more preferably 25 to 50 μm, for consistent manufacture of photo-curable dry film, and prevention of wrapping or curling on a take-up roll.

The photo-curable dry film thus obtained may be attached to an electric or electronic part after stripping the protective film therefrom.

After the protective film is stripped off, the photo-curable dry film (i.e., photo-curable resin layer) is placed in close contact with a substrate using a film attachment apparatus. The substrate used herein may be selected from a silicon wafer, silicon wafer for TSV, silicon wafer worked in thin film form by backside polishing, plastic or ceramic substrate, and substrate having a metal (e.g., Cu, Ni or Au) deposited partially or entirely on its surface by ion sputtering or plating. A typical substrate is provided with holes or grooves having an opening width of 10 to 100 μm and a depth of 10 to 120 μm. The film attachment apparatus is preferably a vacuum laminator. The photo-curable dry film is mounted in the film attachment apparatus where the protective film is stripped from the dry film. In the vacuum chamber kept at a predetermined vacuum, the bare photo-curable resin layer of the dry film is closely bonded to the substrate on a table at a predetermined temperature, using a bonding roll under a predetermined pressure. Preferably, the temperature is 60 to 120° C., the pressure is 0 to 5.0 MPa, and the vacuum is 50 to 500 Pa.

The attachment of dry film may be repeated plural times, if necessary to obtain a photo-curable resin layer having the desired thickness. The attachment step is repeated 1 to 10 times, for example, before a photo-curable resin layer having a thickness of 10 to 1,000 μm, preferably 100 to 500 μm is obtainable.

The assembly of the photo-curable resin layer on the substrate may be prebaked, if necessary, for facilitating photo-cure reaction of the photo-curable resin layer or enhancing the adhesion between the photo-curable resin layer and the substrate. Prebake may be, for example, at 40 to 140° C. for 1 minute to 1 hour. Like the photo-curable resin composition, the photo-curable resin layer attached to the substrate may be subjected to exposure, development, and optionally substrate bonding and post-cure or heat treatment. It is noted that the support film of the photo-curable dry film may be removed before prebake or before PEB, by mechanical stripping or the like, depending on a particular process.

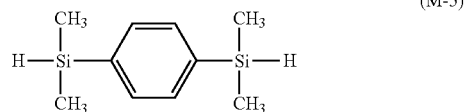
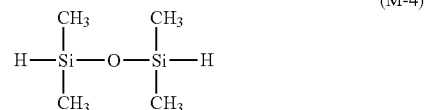
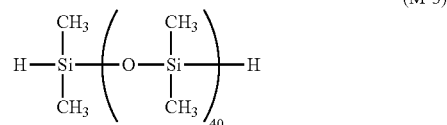
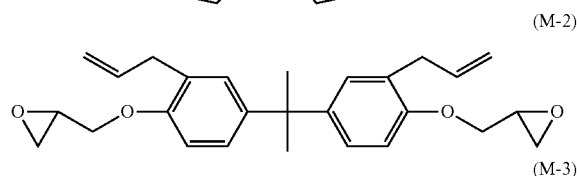
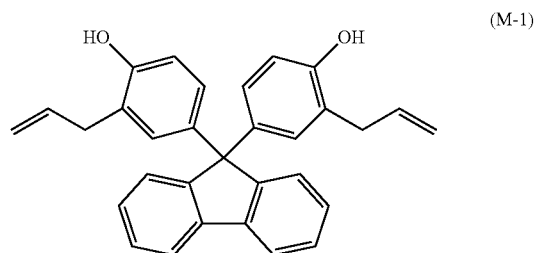
The cured film obtained from the photo-curable resin composition or photo-curable dry film has excellent properties including heat resistance, flexibility, electric insulation, mechanical properties, and substrate adhesion and is thus best suited as protective film for electric and electronic parts such as semiconductor devices.

#### EXAMPLE

Synthesis Examples, Examples and Comparative Example are given below by way of illustration and not by way of limitation. All parts are by weight (pbw).

20

In Synthesis Examples below, compounds M-1 to M-5 having the chemical structure shown below were used.

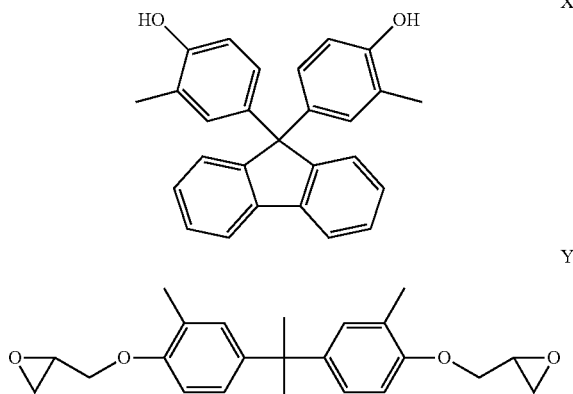


#### Synthesis Example 1

In a 5-L flask equipped with a stirrer, thermometer, nitrogen purging line and reflux condenser, 405.0 g of compound M-1 and 40.0 g of compound M-2 were dissolved in 1,875 g of toluene. To the solution, 949.6 g of compound M-3 and 6.1 g of compound M-4 were added, and it was heated at 60° C. To the flask, 2.2 g of platinum-on-carbon catalyst (5 wt %) was admitted whereupon the internal reaction temperature rose to 65-67° C. After confirmation of this temperature rise, the flask was heated at 90° C. for 3 hours and cooled to 60° C. again. To the flask, 2.2 g of platinum-on-carbon catalyst (5 wt %) was admitted, and 107.5 g of compound M-5 was added dropwise over one hour. At this point, the flask internal temperature rose to 78° C. After the dropwise addition, the reaction solution was ripened for 3 hours at 90° C. and then cooled to room temperature. Then 1,700 g of methyl isobutyl ketone was added. The reaction solution was filtered through a filter under pressure to remove the platinum catalyst. To the polymer solution thus obtained, 760 g of deionized water was added, followed by stirring and stationary holding for separation. The lower layer or water layer was removed. This washing/separatory operation was repeated 6 times, thereby removing the trace acid value from the polymer solution. The solvent was distilled off in vacuum from the polymer solution

## 21

and instead, 950 g of cyclopentanone was added. This yielded a polymer solution (A-1) in cyclopentanone having a solids concentration of 60 wt %. The polymer in the solution was measured for molecular weight by GPC versus polystyrene standards, finding a Mw of 59,000. The polymer corresponded to formula (1) wherein molar fractions  $a=0.550$ ,  $b=0.358$ ,  $c=0.056$ , and  $d=0.036$  as computed from the molar amounts of reactants charged. X and Y are shown below, and  $m=1$  to 40.



## Synthesis Example 2

In a 5-L flask equipped with a stirrer, thermometer, nitrogen purging line and reflux condenser, 308.7 g of compound M-1 and 136.8 g of compound M-2 were dissolved in 1,875 g of toluene. To the solution, 949.6 g of compound M-3 and 6.1 g of compound M-4 were added, and it was heated at 60° C. To the flask, 2.2 g of platinum-on-carbon catalyst (5 wt %) was admitted whereupon the internal reaction temperature rose to 65-67° C. After confirmation of this temperature rise, the flask was heated at 90° C. for 3 hours and cooled to 60° C. again. To the flask, 2.2 g of platinum-on-carbon catalyst (5 wt %) was admitted, and 107.3 g of compound M-5 was added dropwise over one hour. At this point, the flask internal temperature rose to 80° C. After the dropwise addition, the reaction solution was ripened for 3 hours at 90° C. and then cooled to room temperature. Then 1,700 g of methyl isobutyl ketone was added. The reaction solution was filtered through a filter under pressure to remove the platinum catalyst. To the polymer solution thus obtained, 760 g of deionized water was added, followed by stirring and stationary holding for separation. The lower layer or water layer was removed. This washing/separatory operation was repeated 6 times, thereby removing the trace acid value from the polymer solution. The solvent was distilled off in vacuum from the polymer solution and instead, 900 g of cyclopentanone was added. This yielded a polymer solution (A-2) in cyclopentanone having a solids concentration of 60 wt %. The polymer in the solution was measured for molecular weight by GPC versus polystyrene standards, finding a Mw of 55,000. The polymer corresponded to formula (1) wherein molar fractions  $a=0.417$ ,

## 22

$b=0.271$ ,  $c=0.189$ , and  $d=0.123$  as computed from the molar amounts of reactants charged. X, Y and m are as in Synthesis Example 1.

## Synthesis Example 3

In a 5-L flask equipped with a stirrer, thermometer, nitrogen purging line and reflux condenser, 230.0 g of compound M-1 and 205.0 g of compound M-2 were dissolved in 1,875 g of toluene. To the solution, 949.6 g of compound M-3 and 6.1 g of compound M-4 were added, and it was heated at 60° C. To the flask, 2.2 g of platinum-on-carbon catalyst (5 wt %) was admitted whereupon the internal reaction temperature rose to 65-67° C. After confirmation of this temperature rise, the flask was heated at 90° C. for 3 hours and cooled to 60° C. again. To the flask, 2.2 g of platinum-on-carbon catalyst (5 wt %) was admitted, and 107.5 g of compound M-5 was added dropwise over one hour. At this point, the flask internal temperature rose to 80° C. After the dropwise addition, the reaction solution was ripened for 3 hours at 90° C. and then cooled to room temperature. Then 1,700 g of methyl isobutyl ketone was added. The reaction solution was filtered through a filter under pressure to remove the platinum catalyst. To the polymer solution thus obtained, 760 g of deionized water was added, followed by stirring and stationary holding for separation. The lower layer or water layer was removed. This washing/separatory operation was repeated 6 times, thereby removing the trace acid value from the polymer solution. The solvent was distilled off in vacuum from the polymer solution and instead, 950 g of cyclopentanone was added. This yielded a polymer solution (A-3) in cyclopentanone having a solids concentration of 60 wt %. The polymer in the solution was measured for molecular weight by GPC versus polystyrene standards, finding a Mw of 52,000. The polymer corresponded to formula (1) wherein molar fractions  $a=0.317$ ,  $b=0.206$ ,  $c=0.289$ , and  $d=0.188$  as computed from the molar amounts of reactants charged. X, Y and m are as in Synthesis Example 1.

## Synthesis Example 4

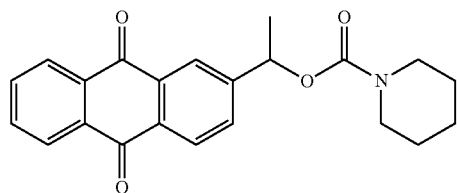
In a 5-L flask equipped with a stirrer, thermometer, nitrogen purging line and reflux condenser, 430.8 g of compound M-2 was dissolved in 1,875 g of toluene. To the solution, 949.6 g of compound M-3 and 6.1 g of compound M-4 were added, and it was heated at 60° C. To the flask, 2.2 g of platinum-on-carbon catalyst (5 wt %) was admitted whereupon the internal reaction temperature rose to 65-67° C. After confirmation of this temperature rise, the flask was heated at 90° C. for 3 hours and cooled to 60° C. again. To the flask, 2.2 g of platinum-on-carbon catalyst (5 wt %) was admitted, and 107.5 g of compound M-5 was added dropwise over one hour. At this point, the flask internal temperature rose to 78° C. After the dropwise addition, the reaction solution was ripened for 5 hours at 90° C. and then cooled to room temperature. Then 1,700 g of methyl isobutyl ketone was added. The reaction solution was filtered through a filter under pressure to remove the platinum catalyst. To the polymer solution thus obtained, 760 g of deionized water was added, followed by

## 23

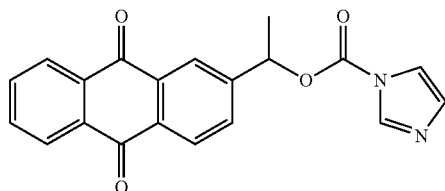
stirring and stationary holding for separation. The lower layer or water layer was removed. This washing/separatory operation was repeated 6 times, thereby removing the trace acid value from the polymer solution. The solvent was distilled off in vacuum from the polymer solution and instead, 950 g of cyclopentanone was added. This yielded a polymer solution (A-4) in cyclopentanone having a solids concentration of 60 wt %. The polymer in the solution was measured for molecular weight by GPC versus polystyrene standards, finding a Mw of 48,000. The polymer corresponded to formula (1) wherein molar fractions a=0, b=0, c=0.606, and d=0.394 as computed from the molar amounts of reactants charged. X, Y and m are as in Synthesis Example 1.

The PBGs and PAG used in Examples and Comparative Example and reported in Table 1 are identified below.

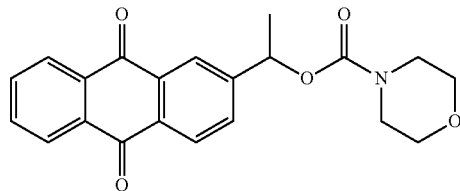
(PBG-1)



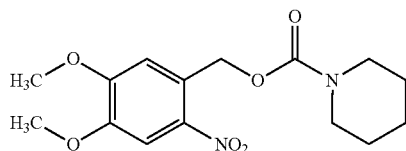
(PBG-2)



(PBG-3)



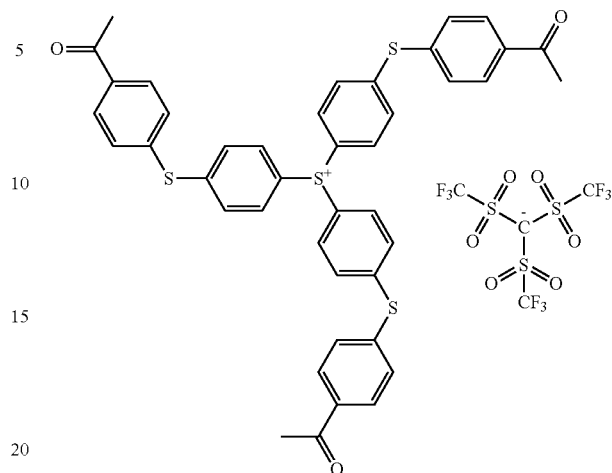
(PBG-4)



## 24

-continued

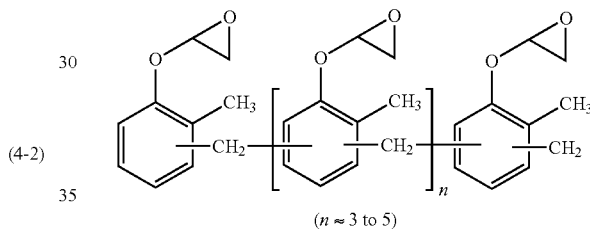
(PAG-1)



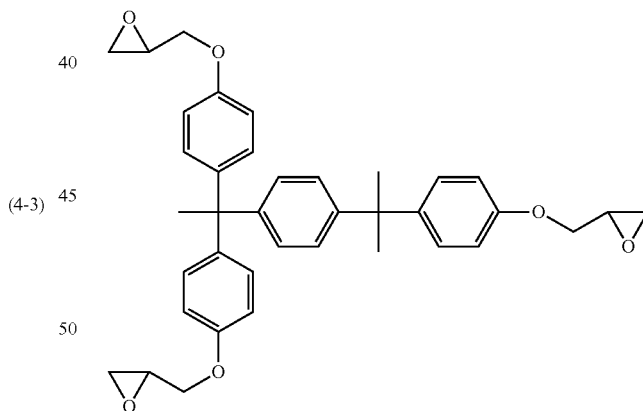
(4-1)

The crosslinkers used in Examples and Comparative Example and reported in Table 1 are identified below.

(EP-1)



(EP-2)



(4-3)

(4-4)

Examples 1 to 9 and Comparative Example 1

Photo-curable resin compositions were prepared by combining the silicone-containing polymer, photobase generator or photoacid generator, crosslinker, and solvent in accordance with the formulation shown in Table 1, stirring and mixing at room temperature until dissolution, and precision filtering through a Teflon® filter with a pore size of 0.2 μm.

TABLE 1

	Photo-curable resin composition (parts by weight)					Resin layer thickness (μm)
	Silicone-containing polymer	Photobase generator	Photoacid generator	Crosslinker	Solvent	
Example 1	A-1	PBG-1		EP-2	cyclopentanone	50
	100 pbw	10 pbw		10 pbw	120 pbw	
Example 2	A-2	PBG-1		EP-1	cyclopentanone	51
	100 pbw	10 pbw		10 pbw	120 pbw	
Example 3	A-2	PBG-1		EP-2	cyclopentanone	50
	100 pbw	10 pbw		10 pbw	120 pbw	
Example 4	A-3	PBG-1		EP-1	cyclopentanone	50
	100 pbw	10 pbw		10 pbw	120 pbw	
Example 5	A-3	PBG-2		EP-2	cyclopentanone	51
	100 pbw	10 pbw		10 pbw	120 pbw	
Example 6	A-3	PBG-3		EP-2	cyclopentanone	53
	100 pbw	10 pbw		10 pbw	120 pbw	
Example 7	A-1	PBG-1		EP-2	cyclopentanone	50
	100 pbw	3 pbw		10 pbw	120 pbw	
Example 8	A-1	PBG-4		EP-2	cyclopentanone	51
	100 pbw	10 pbw		10 pbw	120 pbw	
Example 9	A-4	PBG-1			cyclopentanone	48
	100 pbw	10 pbw			120 pbw	
Comparative Example 1	A-2		PAG-1	EP-2	cyclopentanone	49
	100 pbw		3 pbw	10 pbw	120 pbw	

A die coater was used as the film coater and a polyethylene terephthalate (PET) film of 38 μm thick used as the support film. Each of photo-curable resin compositions of Examples 1 to 9 and Comparative Example 1 was coated onto the support film. The coated film was passed through a hot air circulating oven (length 4 m) set at 100° C. over 5 minutes, forming a photo-curable resin layer on the support film. Using a laminating roll, a polyethylene film of 50 μm thick as the protective film was bonded to the photo-curable resin layer under a pressure of 1 MPa, yielding a photo-curable dry film. The thickness of photo-curable resin layer in Examples and Comparative Example is tabulated in Table 1. The layer thickness was measured by an optical interference film thickness gauge.

Separately, a viscosity was measured by a rheometer MARS II (HAAKE, Germany), specifically by sandwiching a photo-curable resin layer between parallel plates such that the resin layer might have a thickness of 0.5 to 1.0 mm, heating the assembly at a temperature of 80, 90, 100, 110 or 120° C., and applying a shear stress at a frequency of 1 Hz. The viscosity measurements are reported in Table 2.

TABLE 2

Temperature  ( ° C.)	Viscosity (Pa · s)									Comparative Example
	Film									
	Example									
	1	2	3	4	5	6	7	8	9	1
80	482	402	573	690	837	470	489	483	430	463
90	210	175	246	303	361	205	215	211	191	201
100	102	85	121	146	175	100	105	103	91	98
110	56	40	62	76	92	52	58	56	44	50
120	30	21	34	41	52	24	32	31	22	23

From each of the photo-curable dry films of Examples and Comparative Example, the protective film was stripped off. Using a vacuum laminator TEAM-100RF (Takatori Corp.) with a vacuum chamber set at a vacuum of 80 Pa, the photo-curable resin layer on the support film was closely bonded to a migration test substrate (comb-shaped electrode-bearing

substrate, conductor: copper, conductor spacing and width: 20 μm, conductor thickness: 4 μm). The temperature was 110° C. After restoration of atmospheric pressure, the substrate was taken out of the laminator, and the support film was stripped off.

Then the photo-curable resin layer was prebaked on a hot plate at 130° C. for 5 minutes for enhancing adhesion to the substrate. Next, using a contact aligner exposure tool, the photo-curable resin layer was exposed to radiation of 405 nm through a mask. The substrate was baked (PEB) on a hot plate at 130° C. for 10 minutes and cooled. This was followed by spray development in propylene glycol monomethyl ether acetate (PGMEA) for 300 seconds for forming a pattern of the resin layer. The patterned layer on the substrate was post-cured in an oven at 180° C. for 2 hours while the oven was purged with nitrogen.

With respect to pattern forming condition, the exposure dose (mJ/cm<sup>2</sup>) at which a pattern could be formed is reported as sensitivity in Table 3. The resin layer from which no pattern could be formed by using the contact aligner exposure tool and effecting exposure in a dose of 8,000 mJ/cm<sup>2</sup> is rated “NG” in the sensitivity column.

For the evaluation of electrical properties (dielectric breakdown strength), a plurality of photo-curable resin layers of photo-curable dry films were attached to a steel plate under normal pressure and heated in an oven at 180° C. for 2 hours to form a cured film of 0.2 mm thick. The cured film was tested by a breakdown tester TM-5031AM (Tamadensoku

27

Co., Ltd.) to determine the dielectric breakdown strength of a cured coating of a photo-curable resin composition.

A copper migration test included a temperature 85° C., a humidity 85% and an applied voltage 10 V. A time passed until short-circuit was measured, with the upper limit being 1,000 hours.

Table 3 shows the test results of photo-curable dry films of Examples and Comparative Example.

TABLE 3

	Electric properties Dielectric breakdown strength (V/μm)	Pattern forming condition Sensitivity (mJ/cm <sup>2</sup> )	Copper migration Short-circuit time (hr)
Example 1	520	3,800	1,000*
Example 2	570	4,000	1,000*
Example 3	510	4,500	1,000*
Example 4	565	3,900	1,000*
Example 5	520	5,200	1,000*
Example 6	537	6,000	1,000*
Example 7	518	7,700	1,000*
Example 8	507	7,100	1,000*
Example 9	550	3,900	1,000*
Comparative Example 1	420	1,500	250

\*no short-circuiting

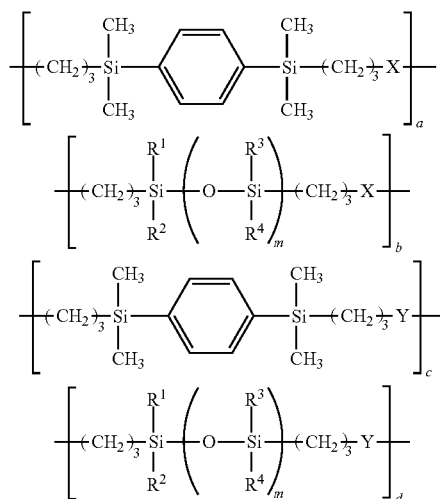
Japanese Patent Application No. 2013-018067 is incorporated herein by reference.

Although some preferred embodiments have been described, many modifications and variations may be made thereto in light of the above teachings. It is therefore to be understood that the invention may be practiced otherwise than as specifically described without departing from the scope of the appended claims.

The invention claimed is:

1. A photo-curable resin composition comprising

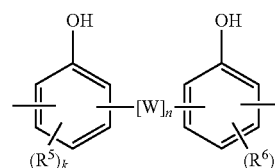
(A) a silicone-containing polymer comprising recurring units of the general formula (1) and having a weight average molecular weight of 3,000 to 500,000,



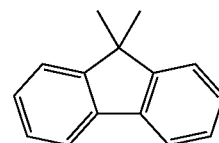
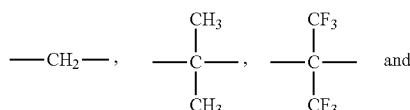
wherein R<sup>1</sup> to R<sup>4</sup> are each independently a monovalent C<sub>1</sub>-C<sub>8</sub> hydrocarbon group, m is an integer of 1 to 100, a, b, c and d each are 0 or a positive number, a+b+c+d=1, X is a divalent

28

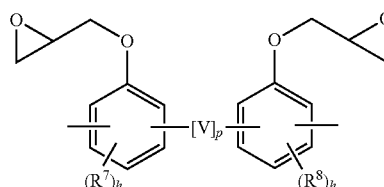
organic group of the general formula (2), and Y is a divalent organic group of the general formula (3),



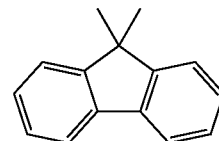
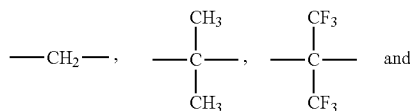
wherein W is a divalent organic group selected from the following:



n is 0 or 1, R<sup>5</sup> and R<sup>6</sup> are each independently a C<sub>1</sub>-C<sub>4</sub> alkyl or alkoxy group, k is independently 0, 1 or 2,



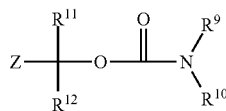
wherein V is a divalent organic group selected from the following:



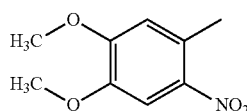
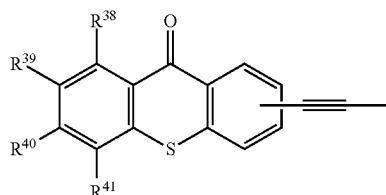
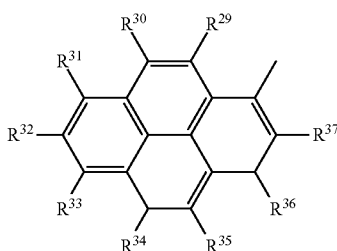
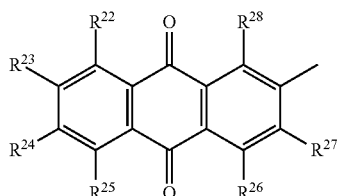
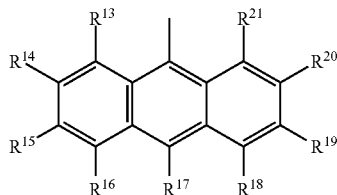
p is 0 or 1, R<sup>7</sup> and R<sup>8</sup> are each independently a C<sub>1</sub>-C<sub>4</sub> alkyl or alkoxy group, and h is independently 0, 1 or 2,

(B) a photobase generator of the general formula (4) which is decomposed with radiation of wavelength 190 to 500 nm to generate a base,

29



wherein  $R^9$  and  $R^{10}$  are each independently hydrogen or a straight, branched or cyclic  $C_1$ - $C_{10}$  alkyl group, or  $R^9$  and  $R^{10}$  may bond together to form a nitrogen-containing aliphatic or aromatic ring of 3 to 8 carbon atoms with the nitrogen atom to which they are attached, which ring may have a substituent or contain a heteroatom,  $R^{11}$  and  $R^{12}$  are each independently hydrogen, a straight, branched or cyclic  $C_1$ - $C_{10}$  alkyl group or an optionally substituted phenyl group, Z is a monovalent organic group selected from the general formulae (Z-1) to (Z-4) and (Z-12):



wherein  $R^{13}$  to  $R^{45}$  are each independently selected from the class consisting of hydrogen, halogen, an optionally substituted, straight, branched or cyclic  $C_1$ - $C_{10}$  alkyl group, optionally substituted  $C_1$ - $C_6$  alkoxy group, optionally substituted

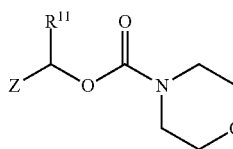
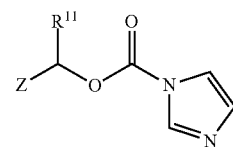
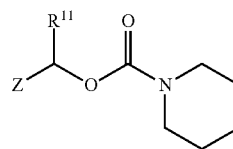
30

$C_2$ - $C_6$  alkenyl group, optionally substituted  $C_2$ - $C_6$  alkynyl group, and optionally substituted  $C_6$ - $C_{10}$  aryl group, and (C) a solvent.

- (4) 2. The composition of claim 1 wherein in formula (1), c and d are not equal to 0 at the same time, and  $0 < (c+d) \leq 1.0$ .

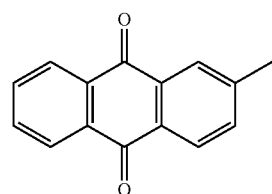
3. The composition of claim 1, further comprising (D) an epoxy compound containing on average at least two epoxy groups per molecule other than component (A) as crosslinker.

4. The composition of claim 1 wherein the photobase generator having formula (4) is selected from the general formulae (4-11) to (4-13):

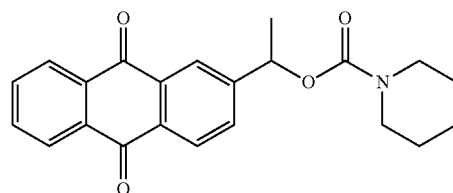


wherein Z is as defined above,  $R^{11}$  is hydrogen, a straight, branched or cyclic  $C_1$ - $C_{10}$  alkyl group or an optionally substituted phenyl group.

5. The composition of claim 1 wherein in formula (4), Z is a group having the following formula (Z-11):



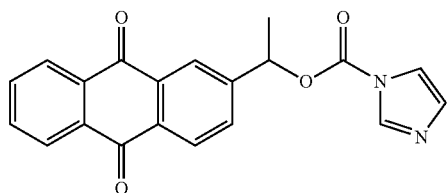
6. The composition of claim 1 wherein the photobase generator having formula (4) is selected from the following formulae (4-1) to (4-4):



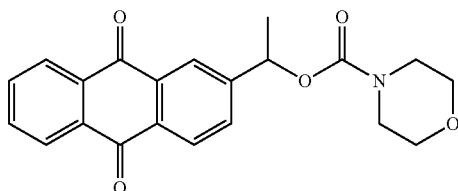


31

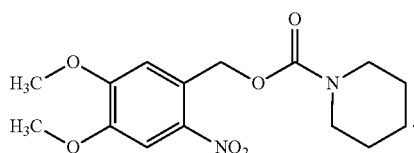
-continued



(4-2)



(4-3)



(4-4)

7. A photo-curable dry film obtained by coating and drying the photo-curable resin composition of claim 1 to a support film.

8. A pattern forming process comprising the steps of:

- (i) applying the photo-curable dry film of claim 7 to a substrate to form a photo-curable resin layer thereon,
- (ii) exposing the photo-curable resin layer to radiation of wavelength 190 to 500 nm through a photomask, and
- (iii) baking the exposed resin layer and developing it in a developer.

9. The process of claim 8, further comprising the step (iv) of post-curing the patterned resin layer at a temperature of 100 to 250° C.

10. A film for the protection of electric and electronic parts, which is the cured layer obtained by the process of claim 8.

11. An electric or electronic part comprising the protective film of claim 10.

12. A pattern forming process comprising the steps of:

- (i) applying the photo-curable resin composition of claim 1 to a substrate to form a photo-curable resin layer thereon,
- (ii) exposing the photo-curable resin layer to radiation of wavelength 190 to 500 nm through a photomask, and
- (iii) baking the exposed resin layer and developing it in a developer.

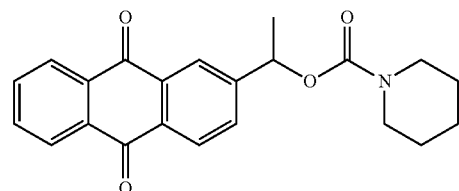
13. The process of claim 12, further comprising the step (iv) of post-curing the patterned resin layer at a temperature of 100 to 250° C.

32

14. A film for the protection of electric and electronic parts, which is the cured layer obtained by the process of claim 12.

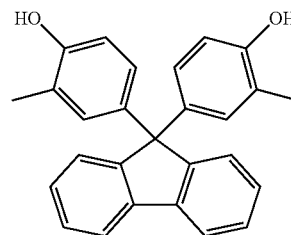
15. An electric or electronic part comprising the protective film of claim 14.

16. The composition of claim 1, wherein the photobase generator having formula (4) is

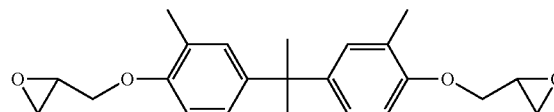


(4-1)

17. The composition of claim 16, wherein:



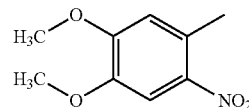
X



Y

and m is 1 to 40.

18. The composition of claim 1 wherein in formula (4), Z is a group having the following formula (Z-12):



(Z-12)

\* \* \* \* \*